CLAIMS:

1. A thermally activatable antioxidant precursor compound of the formula:

A—B

wherein A and B are the same or different, each consisting of a moiety other than a hydrogen atom; and

wherein A and B are connected via a labile bond, and are able to dissociate through breakage of the labile bond upon exposure of said compound to a predetermined temperature shift from a lower temperature to a higher temperature, thereby to generate corresponding free radicals A• and B• at least one of which being suitable for use as an antioxidant.

2. The thermally activatable antioxidant precursor compound of claim 1, wherein each of A and B comprises a monocyclic aromatic or polycyclic aromatic ring system, optionally substituted at one or more positions.

3. The thermally activatable antioxidant precursor compound of claim 1, wherein the labile bond is a carbon-carbon bond and each of the free radicals A• and B• is a carbon centered free radical.

4. The thermally activatable antioxidant precursor compound of claim 1, wherein the compound A-B is a dimer and each of the free radicals A• and B• is a monomer.

5. The thermally activatable antioxidant precursor compound of claim 1, wherein each of free radicals A• and B• are suitable for use as an antioxidant.

6. The thermally activatable antioxidant precursor compound of claim 2, wherein each of A and B further comprise a heterocyclic ring.

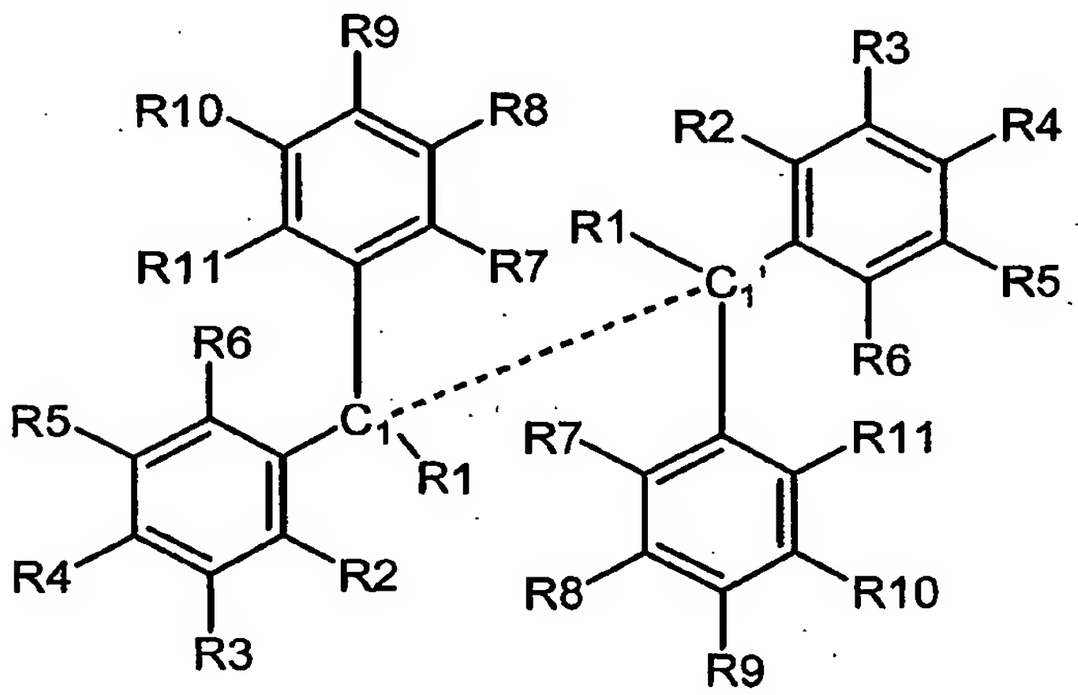
7. The thermally activatable antioxidant precursor compound of claim 1, wherein the free radicals A• and B• are able to re-associate through the formation of a labile bond upon exposure of said radicals to a predetermined temperature shift from a higher temperature to a lower temperature thereby to regenerate the corresponding antioxidant precursor compound of the formula:

A—B

8. The thermally activatable antioxidant precursor compound of claim 6, wherein the compound A-B is a dimer and each of the free radicals A• and B• are monomers.

9. The thermally activatable antioxidant precursor compound of claim 1, wherein A and B are identical.

10. The thermally activatable antioxidant precursor compound of claim 1, wherein the compound A-B is selected from compounds of the formula X:



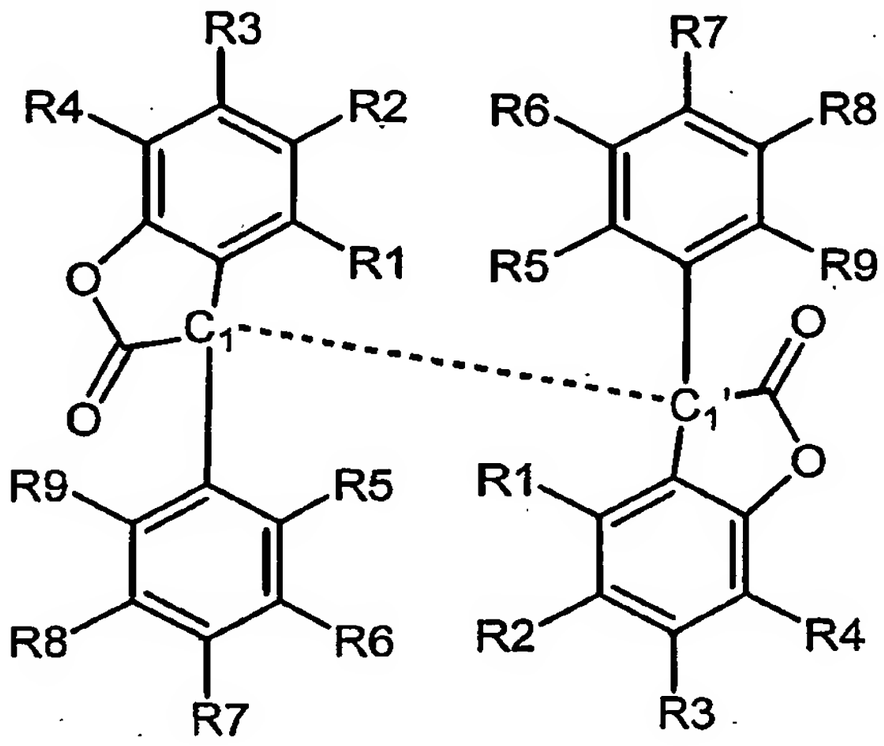
X

wherein the dashed line represents the labile bond susceptible to breakage upon exposure of said compound to a temperature shift from a lower temperature to a higher temperature; and

wherein R1-R11 are the same or different, each independently selected from hydrogen or a substituent selected from the following group: linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituant selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), NO_2, C_5-C_8 cycloalkyl optionally substituted with one or more C_1-C_{18} alkyl, and C_6-C_{20} aryl, optionally substituted with one or more C_1-C_{18} alkyl,

and wherein optionally any two of R2 to R11 within the same moiety of A or B may be linked to form a substituted or unsubstituted bicyclic or polycyclic fusedring system, and wherein optionally R1 may be linked to one or more of R2, R6, R7, and R11 within the same moiety of A or B, to form a substituted or unsubstituted bicyclic or polycyclic fused ring system optionally comprising one or more heterocyclic rings.

11. The thermally activatable antioxidant precursor compound of claim 1, wherein the compound of the formula A-B has a structure of formula I:

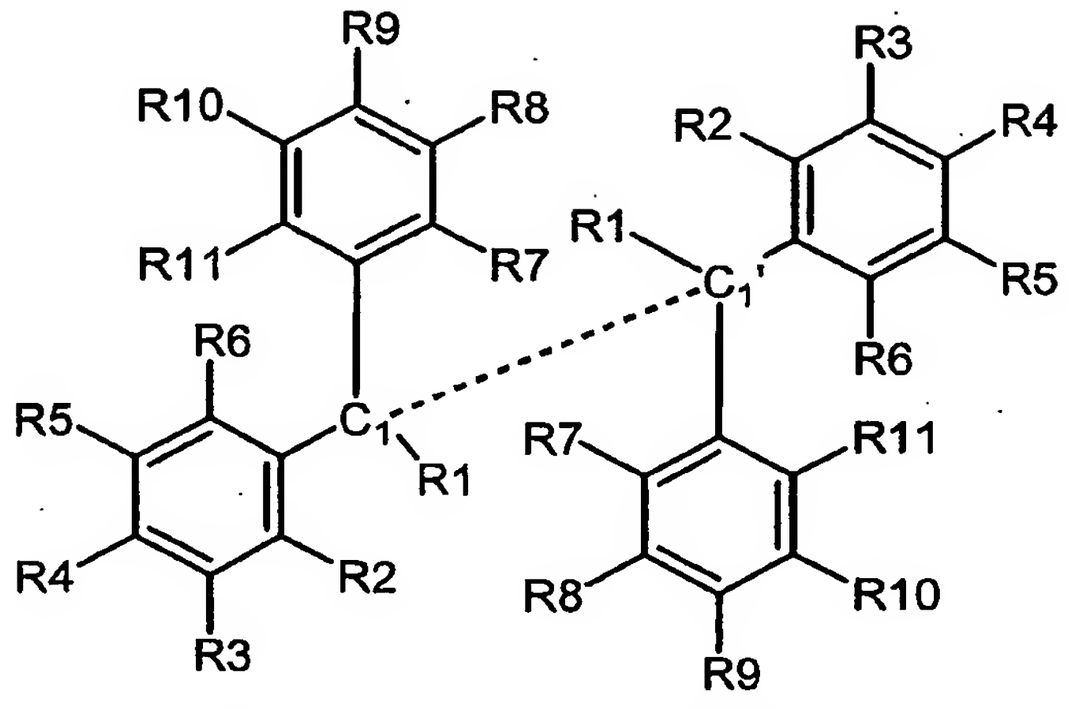


I

wherein the dashed line represents the labile bond susceptible to breakage upon exposure of said compound to a temperature shift from a lower temperature to a higher temperature; and

wherein R1 to R9 are the same or different, each independently selected from hydrogen or a substituent selected from the following group: linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituent selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), NO_2, C_5-C_8 cycloalkyl optionally substituted with one or more C_1-C_{18} alkyl, and C_6-C_{20} aryl, optionally substituted with one or more C_1-C_{18} alkyl.

12. The thermally activatable antioxidant precursor compound of claim 1, wherein the compound of the formula A-B has a structure of formula II:



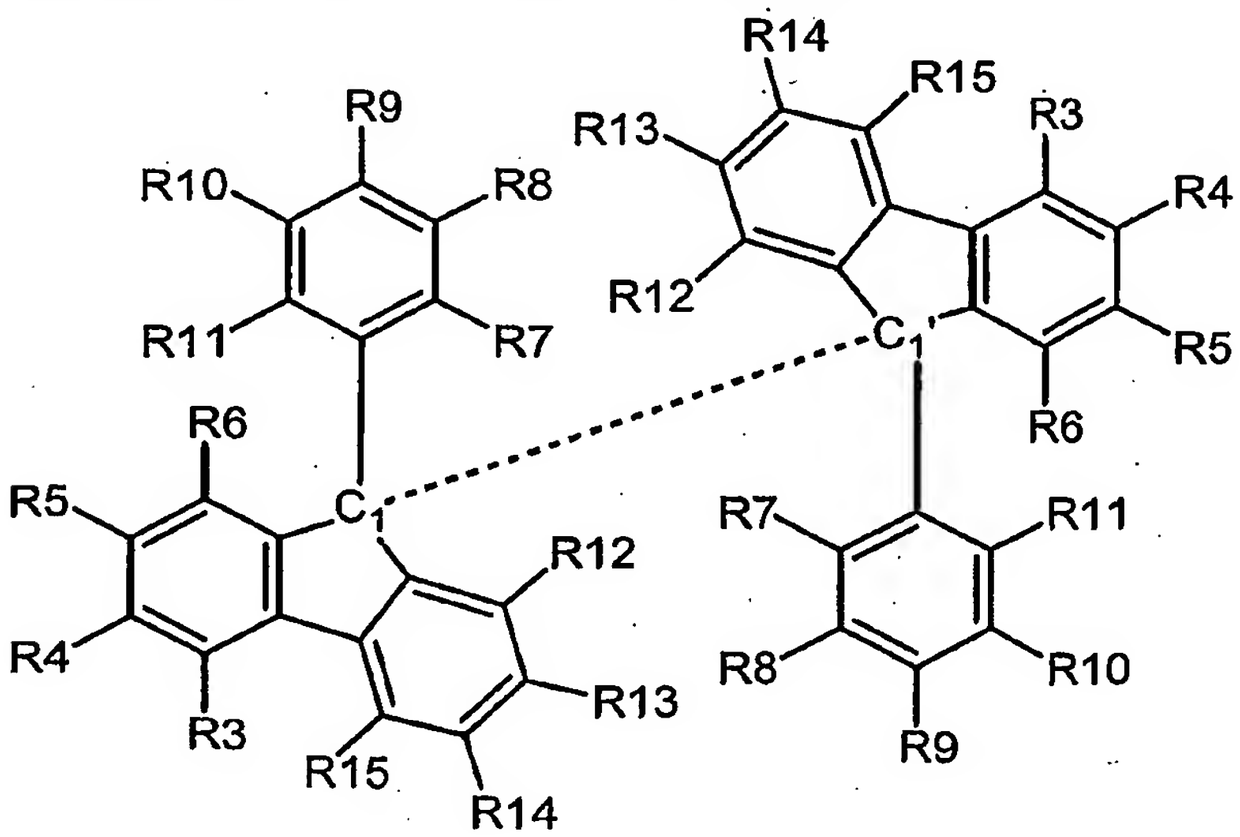
II

wherein the dashed line represents the labile bond susceptible to breakage upon exposure to a higher temperature; and

wherein R1 represents an electron withdrawing group;

R2-R11 are the same or different, each independently selected from hydrogen or a substituent selected from the following group: linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituent selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), NO_2, C_5-C_8 cycloalkyl optionally substituted with one or more C_1-C_{18} alkyl, and C_6-C_{20} aryl, optionally substituted with one or more C_1-C_{18} alkyl.

13. The thermally activatable antioxidant precursor compound of claim 1, wherein the compound of the formula A-B has a structure of formula III:

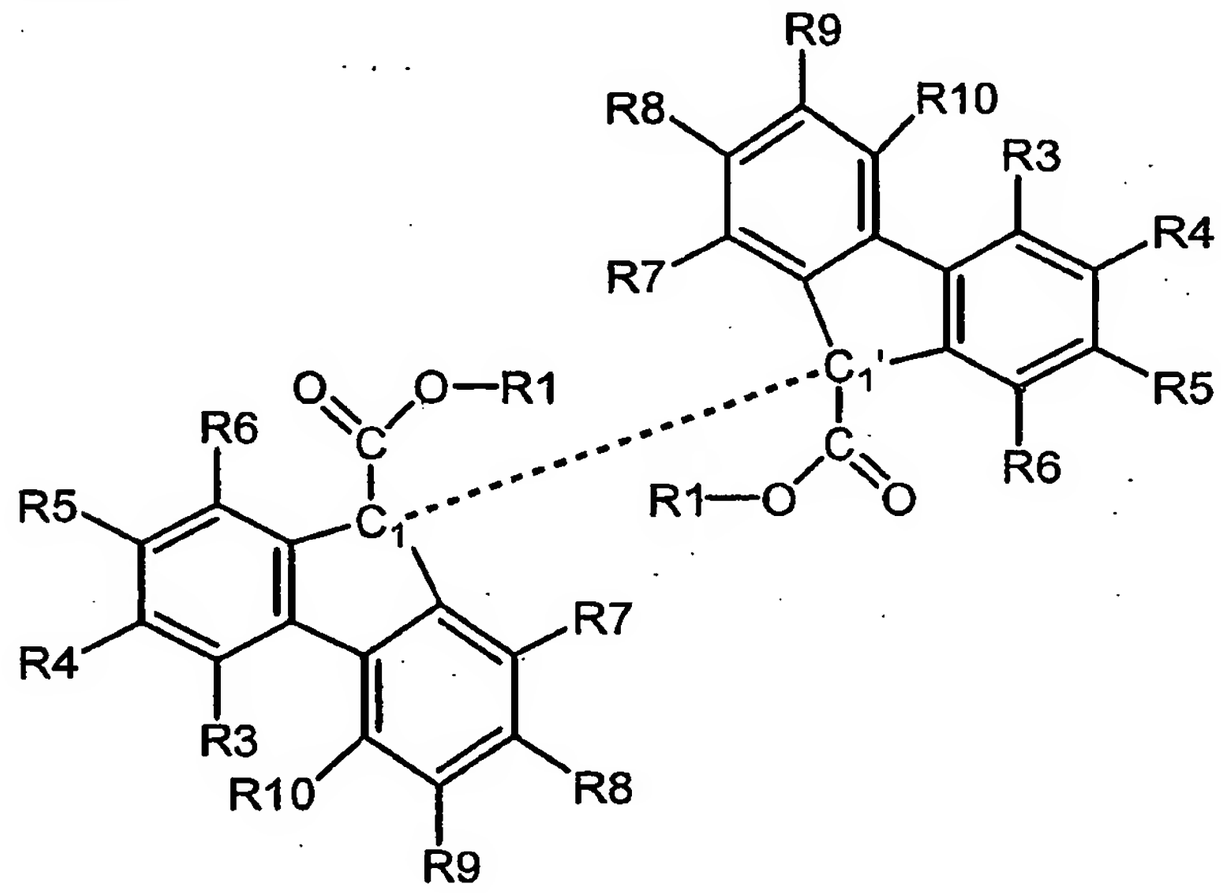


III

wherein the dashed line represents the labile bond susceptible to breakage upon exposure to a higher temperature; and

wherein R3-R15 are the same or different, each independently selected from hydrogen or a substituent selected from the following group: linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituent selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), NO_2, C_5-C_8 cycloalkyl optionally substituted with one or more C_1-C_{18} alkyl, and C_6-C_{20} aryl, optionally substituted with one or more C_1-C_{18} alkyl.

14. The thermally activatable antioxidant precursor compound of claim 1, wherein the compound of the formula A-B has a structure of formula IV:



IV

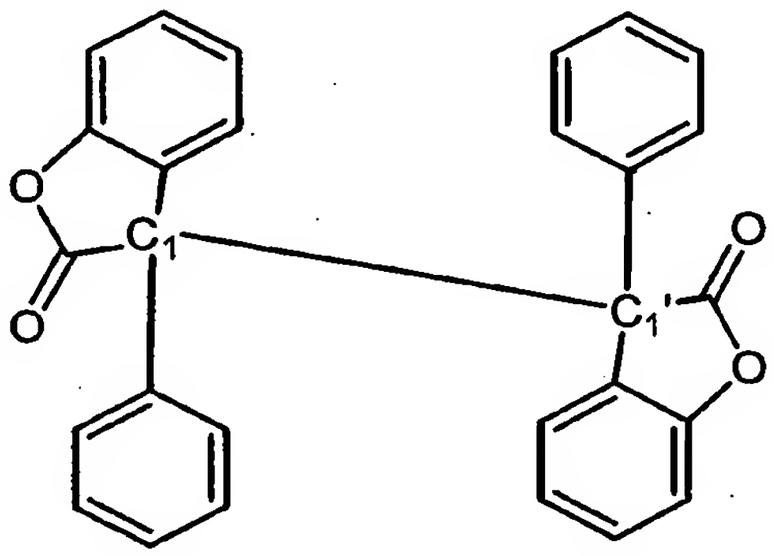
wherein the dashed line represents the labile bond susceptible to breakage upon exposure to a higher temperature; and

wherein R1 and R3-R10 are the same or different, each independently selected from hydrogen or a substituent selected from the following group: linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituent selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), NO_2,

C_5-C_8 cycloalkyl optionally substituted with one or more C_1-C_{18} alkyl, and C_6-C_{20} aryl, optionally substituted with one or more C_1-C_{18} alkyl.

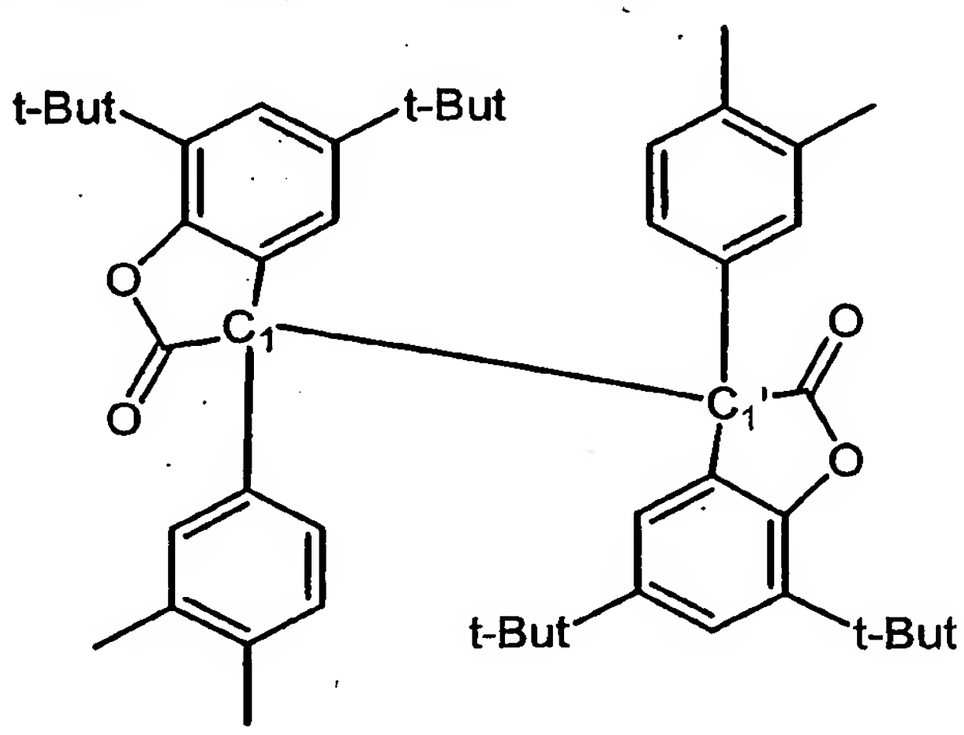
15. The thermally activatable antioxidant precursor compound of claim 12, wherein the electron withdrawing group is selected from CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituent selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), and NO_2.

16. The thermally activatable antioxidant precursor compound of claim 1, wherein the compound has a structure corresponding to formula IA:



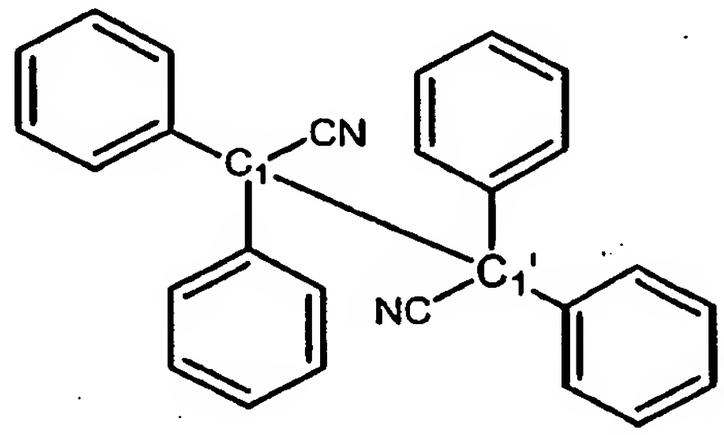
IA

17. The thermally activatable antioxidant precursor compound of claim 1, wherein the compound has a structure corresponding to formula IB:



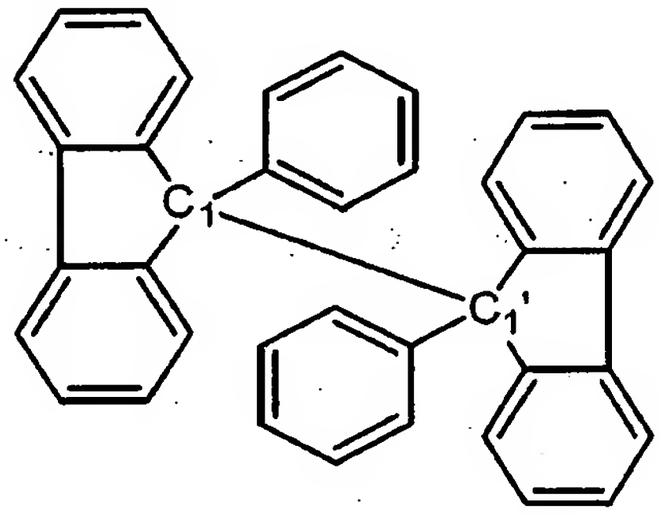
IB

18. The thermally activatable antioxidant precursor compound of claim 1, wherein the compound has a structure corresponding to formula IIA:



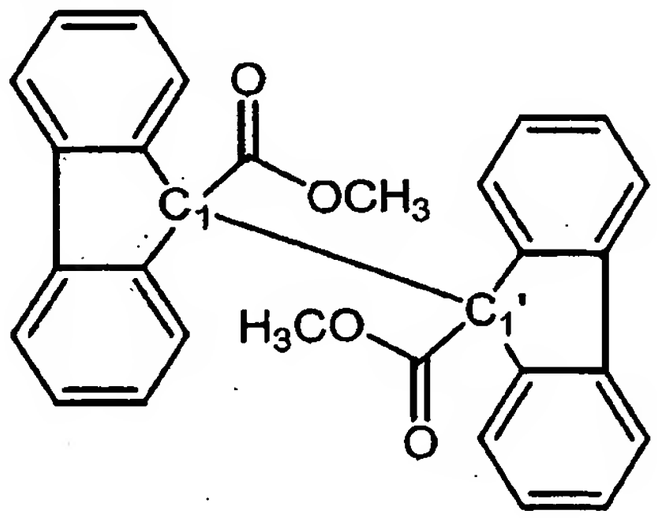
IIA

19. The thermally activatable antioxidant precursor compound of claim 1, wherein the compound has a structure corresponding to formula IIIA:



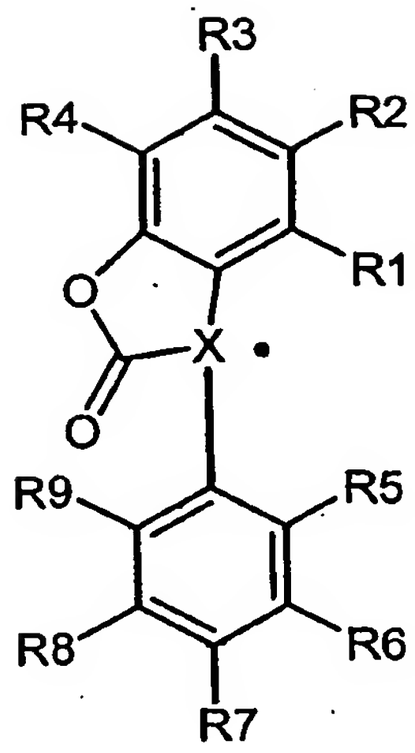
IIIA

20. The thermally activatable antioxidant precursor compound of claim 1, wherein the compound has a structure corresponding to formula IVA:



IVA

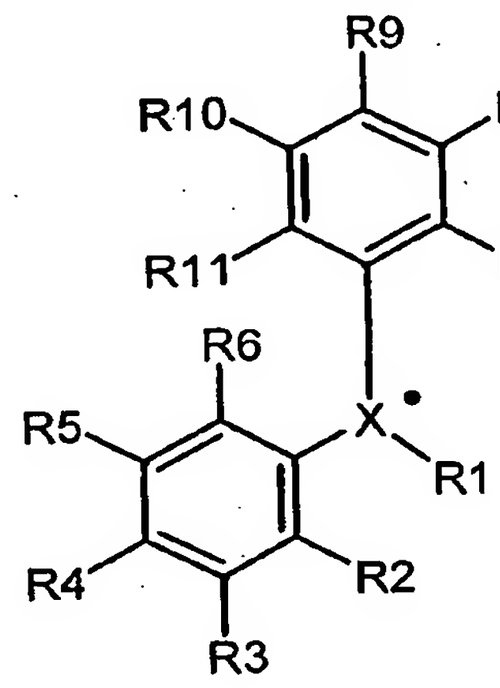
21. The thermally activatable antioxidant precursor compound of claim 1, wherein one of or both of the free radicals A• and B• are of the formula V:



V

wherein X represents C_1 or C_1' and R1 to R9 are the same or different, each independently selected from hydrogen or a substituent selected from the following group: linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituent selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), NO_2, C_5-C_8 cycloalkyl optionally substituted with one or more C_1-C_{18} alkyl, and C_6-C_{20} aryl, optionally substituted with one or more C_1-C_{18} alkyl.

22. The thermally activatable antioxidant precursor compound of claim 1, wherein one of or both of the free radicals A• and B• are of the formula VI:



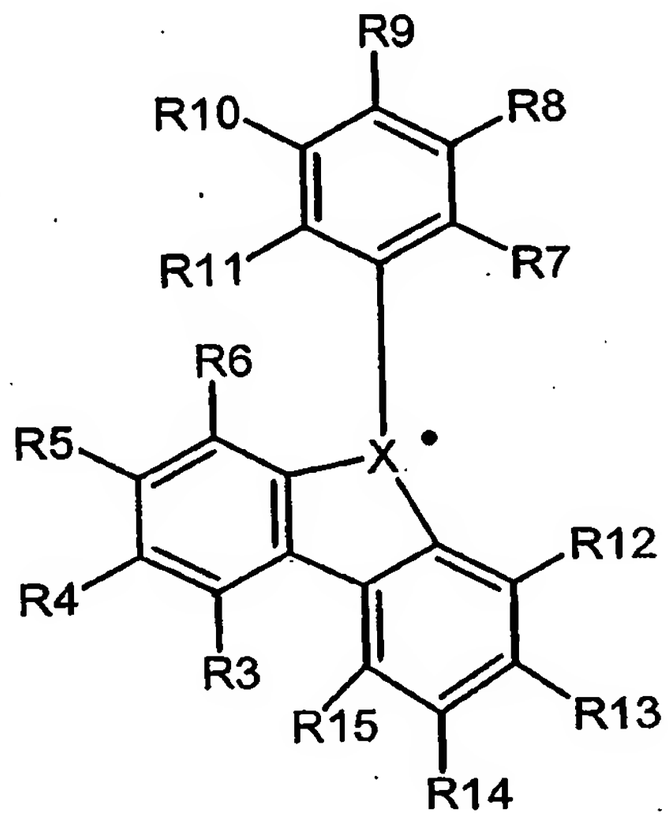
VI

wherein X represents C_1 or C_1' and R1 represents an electron withdrawing group selected from CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituent selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), and NO_2.

and R2 to R11 are the same or different, each independently selected from hydrogen or a substituent selected from the following group: linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituent selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), NO_2, C_5-C_8 cycloalkyl optionally substituted with one or more C_1-C_{18} alkyl, and C_6-C_{20} aryl, optionally substituted with one or more C_1-C_{18} alkyl.

23. The thermally activatable antioxidant precursor compound of claim 22, wherein the C_5 -C_8 cycloalkyl groups carry C_1 -C_{18} alkyl groups as substituents.

24. The thermally activatable antioxidant precursor compound of claim 1, wherein one of or both of the free radicals A• and B• are of the formula VII:

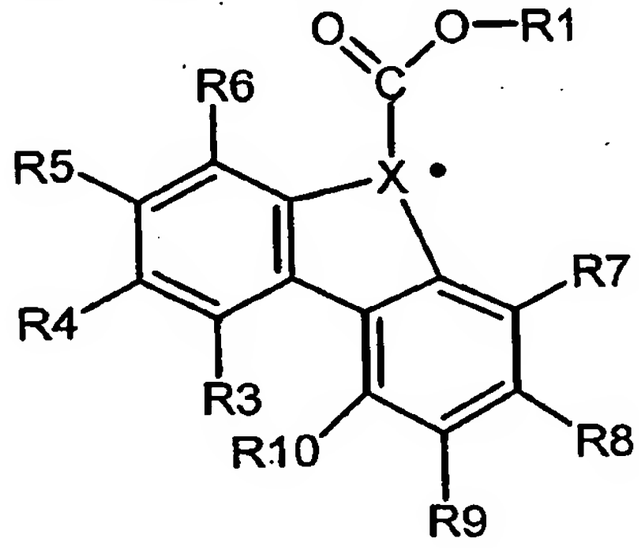


VII

wherein X represents C_1 or C_1' and R3 to R15 are the same or different, each independently selected from hydrogen or a substituent selected from the following group: linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or

branched C_2-C_{18} alkynyl, CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituent selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), NO_2, C_5-C_8 cycloalkyl optionally substituted with one or more C_1-C_{18} alkyl, and C_6-C_{20} aryl, optionally substituted with one or more C_1-C_{18} alkyl.

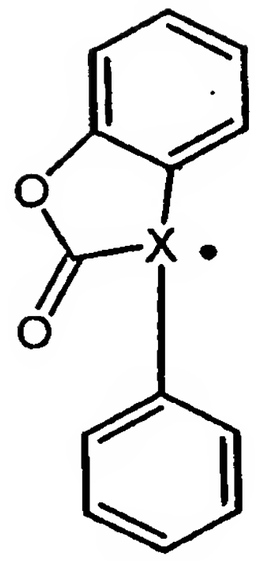
25. The thermally activatable antioxidant precursor compound of claim 1, wherein one of or both of the free radicals A• and B• are of the formula VIII:



VIII

wherein X represents C_1 or C_1' and R1 and R3 to R10 are the same or different, each independently selected from hydrogen or a substituent selected from the following group: linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituent selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), NO_2, C_5-C_8 cycloalkyl optionally substituted with one or more C_1-C_{18} alkyl, and C_6-C_{20} aryl, optionally substituted with one or more C_1-C_{18} alkyl.

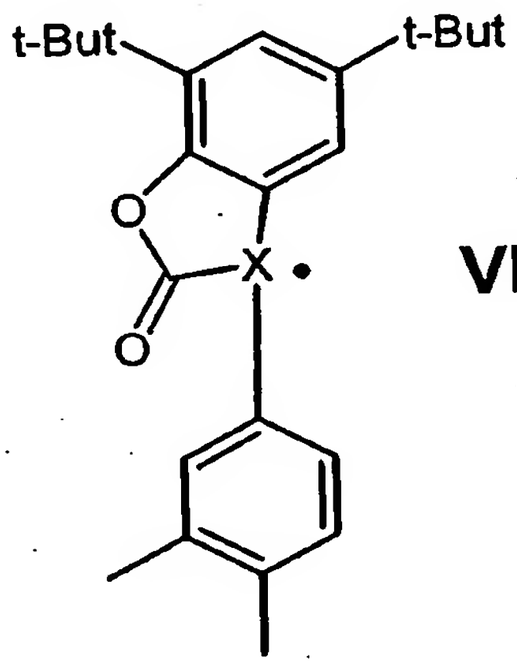
26. The thermally activatable antioxidant precursor compound of claim 1, wherein either or both of the free radicals A• and B• are of the formula VA:



VA

wherein X represents C_1 or C_1'.

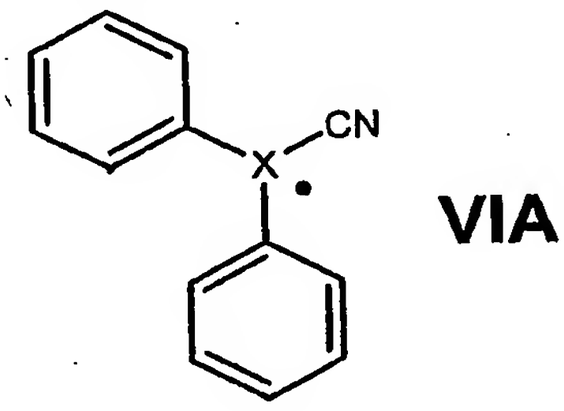
27. The thermally activatable antioxidant precursor compound of claim 1, wherein either or both of the free radicals A• and B• are of the formula VB:



VB

wherein X represents C_1 or C_1'.

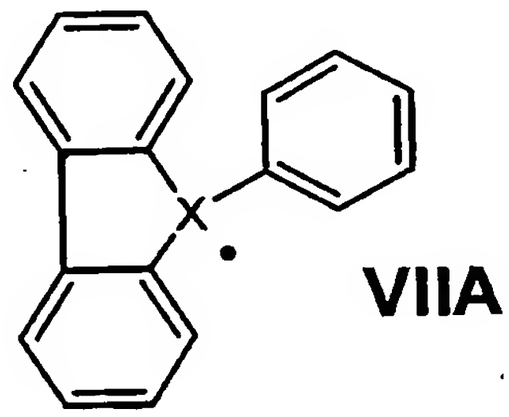
28. The thermally activatable antioxidant precursor compound of claim 1, wherein either or both of the free radicals A• and B• are of the formula VIA:



VIA

wherein X represents C_1 or C_1'.

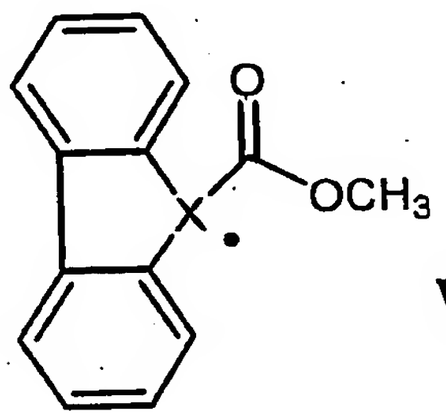
29. The thermally activatable antioxidant precursor compound of claim 1, wherein either or both of the free radicals A• and B• are of the formula VIIA:



VIIA

wherein X represents C_1 or C_1'.

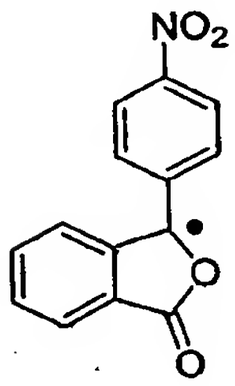
30. The thermally activatable antioxidant precursor compound of claim 1, wherein either or both of the free radicals A• and B• are of the formula VIIIA:



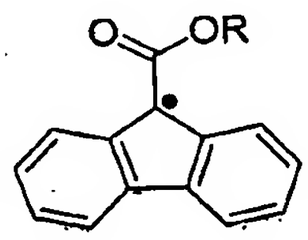
VIIIA

wherein X represents C_1 or C_1'.

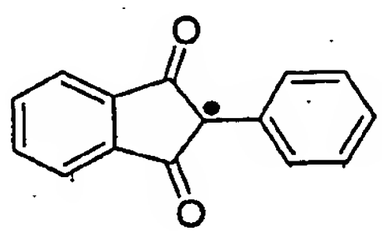
31. The thermally activatable antioxidant precursor compound of claim 1, wherein at least one of A and B is selected from the group consisting of:



,

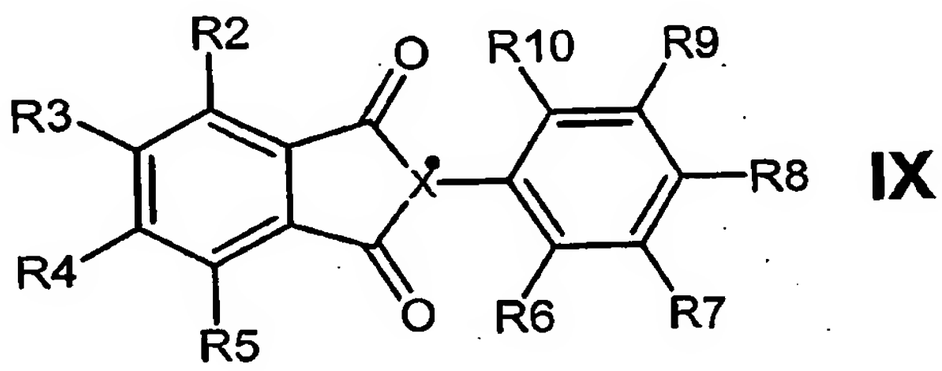


and



wherein R is selected from hydrogen or a substituent selected from the following group: linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituent selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), NO_2, C_5-C_8 cycloalkyl optionally substituted with one or more C_1-C_{18} alkyl, and C_6-C_{20} aryl, optionally substituted with one or more C_1-C_{18} alkyl.

32. The thermally activatable antioxidant precursor compound of claim 1, wherein one of or both of the free radicals A• and B• are of the formula IX:



IX

wherein X represents C_1 or C_1', and R1 to R10 are the same or different, each independently selected from hydrogen or a substituent selected from the following group: linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, CN, $CHal_3$ (where Hal=Cl, Br or F), CO_2R16 (where R16 comprises hydrogen or a substituent selected from a linear or branched C_1-C_{18} alkyl, linear or branched C_2-C_{18} alkenyl, linear or branched C_2-C_{18} alkynyl, C_5-C_8 cycloalkyl, and C_6-C_{20} aryl), NO_2, C_5-C_8 cycloalkyl optionally substituted with one or more C_1-C_{18} alkyl, and C_6-C_{20} aryl, optionally substituted with one or more C_1-C_{18} alkyl.

33. The thermally activatable antioxidant precursor compound of claim 1, with the proviso that the compound is not the compound of formula (11) disclosed in United States Patent 5,367,008 or the compound of formula (10) disclosed in United States

Patent 5,428,177 or the dimeric form of Irganox HP-136 (Ciba Speciality Products) or related dimeric products.

34. The thermally activatable antioxidant precursor compound of claim 1, wherein the bond dissociation energy of the labile bond is less than 80 kcal/mol.

35. The thermally activatable antioxidant precursor compound of claim 34, wherein the bond dissociation energy of the labile bond is less than 50 kcal/mol.

36. The thermally activatable antioxidant precursor compound of claim 35, wherein the bond dissociation energy of the labile bond is less than 25 kcal/mol.

37. The thermally activatable antioxidant precursor compound of claim 36, wherein the bond dissociation energy of the labile bond is less than 20 kcal/mol.

38. The thermally activatable antioxidant compound of claim 1, wherein said temperature shift is from a lower temperature of from 0°C to 40°C to a higher temperature of from 20°C to 400°C.

39. Use of a compound of the formula:

A—B

as defined in any one of claims 1 to 38, as a thermally activatable antioxidant precursor compound.

40. A composition comprising: (a) a compound susceptible to oxidation; and (b) the thermally activatable antioxidant precursor compound of any one of claims 1 to 38.

41. The composition of claim 40, wherein the compound (a) is more susceptible to oxidation at a higher temperature than at a lower temperature.

42. A method for generating an antioxidant, the method comprising the steps of:

a) providing an antioxidant precursor compound of the formula:

A—B

as described in any one of claims 1 to 38; and

b) adjusting the temperature of A-B to thereby cause dissociation of the compound into free radicals A• and B•.

43. The method of claim 42, wherein the step of adjusting comprises shifting the temperature of the antioxidant precursor compound from a lower temperature of from 0°C to 40°C to a higher temperature of from 20°C to 400°C.

44. The method of claim 42, wherein the antioxidant precursor compound is substantially dormant prior to the step b) of adjusting.

45. The method of claim 43 wherein the antioxidant precursor compound can be at least in part reformed at said lower temperature; step b) comprising heating the antioxidant precursor compound to said higher temperature, the method further comprising step c) cooling the free radicals A• and B• formed in step b) to said lower temperature to thereby cause at least partial reassociation of the free radicals A• and B• into the thermally activatable antioxidant precursor compound A-B.

46. The method of claim 45, wherein the free radicals A• and B• are monomers and reassociation comprises dimerization of the free radicals A• and B• to regenerate A-B.

47. A method of preventing or slowing oxidation of at least one molecule susceptible to oxidation in a reaction mixture or target environment, the method comprising the steps of:

a) providing an antioxidant precursor compound of the formula:

A—B

as described in any one of claims 1 to 38;

b) adding the compound to the reaction mixture or target environment; and

c) if necessary adjusting a temperature of the reaction mixture or target environment to a temperature sufficient to cause dissociation of the compound into free radicals A• and B•.

48. The method of claim 47, wherein the step of adjusting comprises shifting the temperature of the antioxidant precursor compound from a lower temperature of from 0°C to 40°C to a higher temperature of from 20°C to 400°C.

49. The method of claim 47, wherein the temperature sufficient to cause dissociation of the compound into free radicals A• and B• is a higher temperature portion of a thermal cycle.

50. The method of claim 49, wherein the antioxidant precursor compound dissociates into the free radicals A• and B• at a temperature lower than a desired temperature for said reaction mixture or target environment.

51. The method of claim 48, wherein the method involves a thermal cycle comprising a lower temperature portion following a higher temperature portion, the method further comprising step d) cooling the reaction mixture or target environment to the lower temperature portion of the thermal cycle thereby to cause at least partial reassociation of A and B to form the thermally activated antioxidant precursor compound A-B.

52. The method of claim 51, wherein the compound A-B is substantially dormant at the lower temperature portion of the thermal cycle.

53. A composition comprising at least one molecule susceptible to oxidation, and two or more compounds according to claim 1, each of said two or more compounds having alternative combinations of moieties A and B.

54. The composition of claim 53, wherein each of said two or more compounds comprises a labile bond having a bond strength that is different from all other compounds of said two or more compounds.

55. The composition according to claim 53, wherein said composition is suitable for subjection to a thermal cycle to cause selective dissociation of moieties A and B for each of said two or more compounds.

56. A method for synthesizing the thermally activatable antioxidant precursor compound of claim 1, the method comprising the steps of:

a) providing a mixture comprising A-H, B-H and tert-butyl peroxide, wherein each H is a hydrogen atom; and

b) performing a photolysis reaction to produce t-BuOH and A-B.

57. The method of claim 53, wherein the moieties A and B are identical.

58. The method of claim 53, wherein photolysis is carried out at 350 nm.

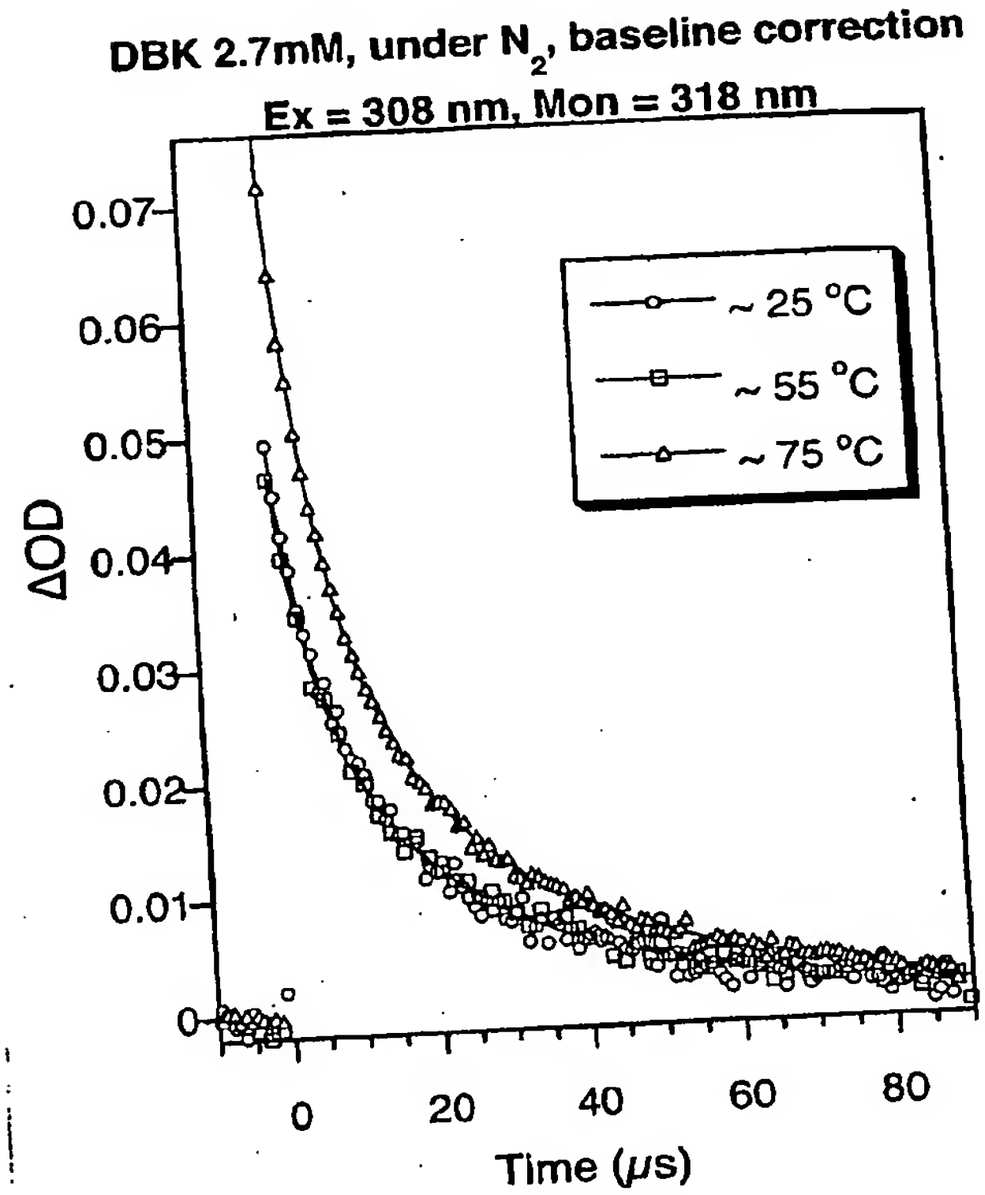

DBK 2.7mM, under N_2, baseline correction
Ex = 308 nm, Mon = 318 nm
~ 25 °C
~ 55 °C
~ 75 °C
ΔOD
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
20
40
60
80
Time (μs)

Figure 1A

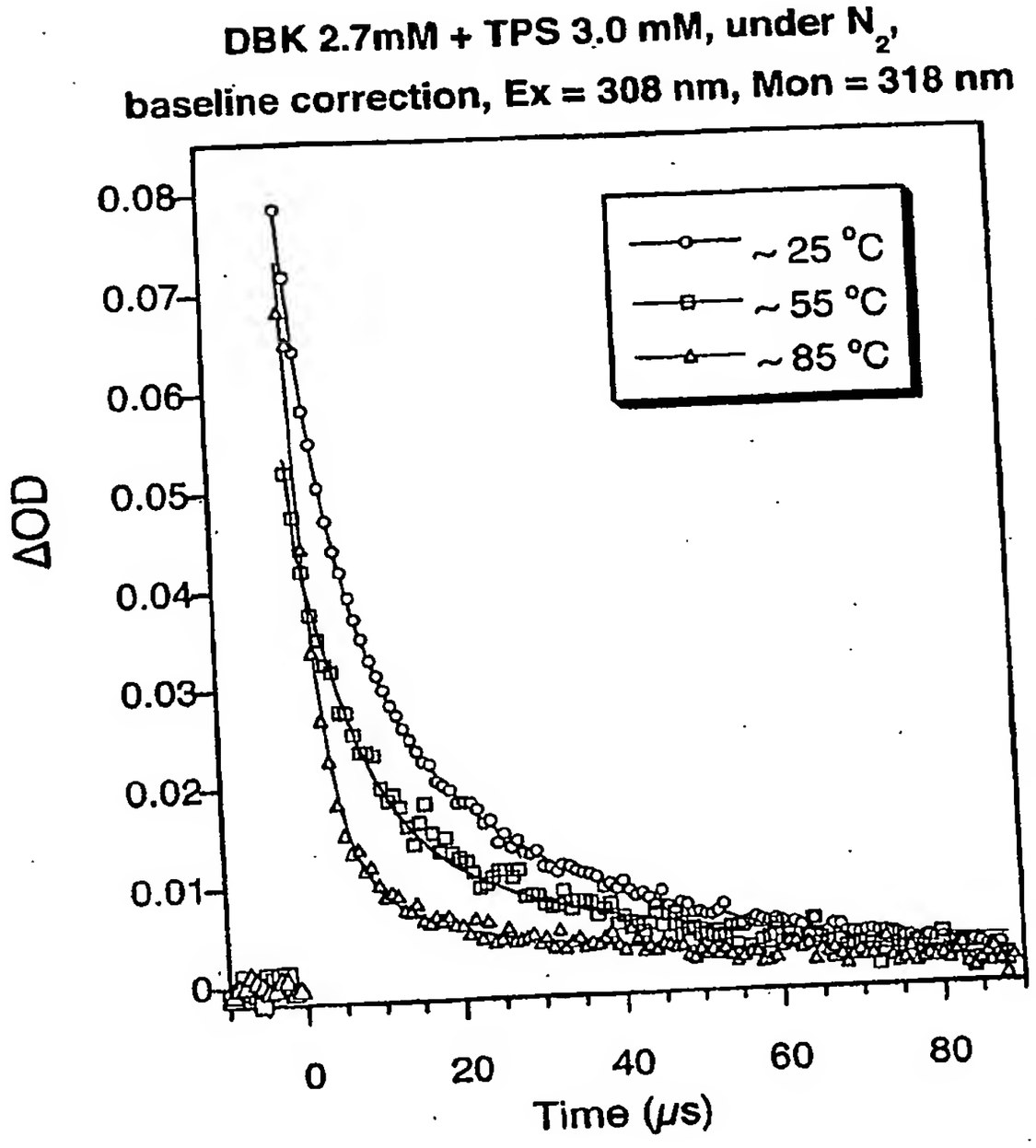

DBK 2.7mM + TPS 3.0 mM, under N_2,
baseline correction, Ex = 308 nm, Mon = 318 nm
~ 25 °C
~ 55 °C
~ 85 °C
ΔOD
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
20
40
60
80
Time (μs)

Figure 1B

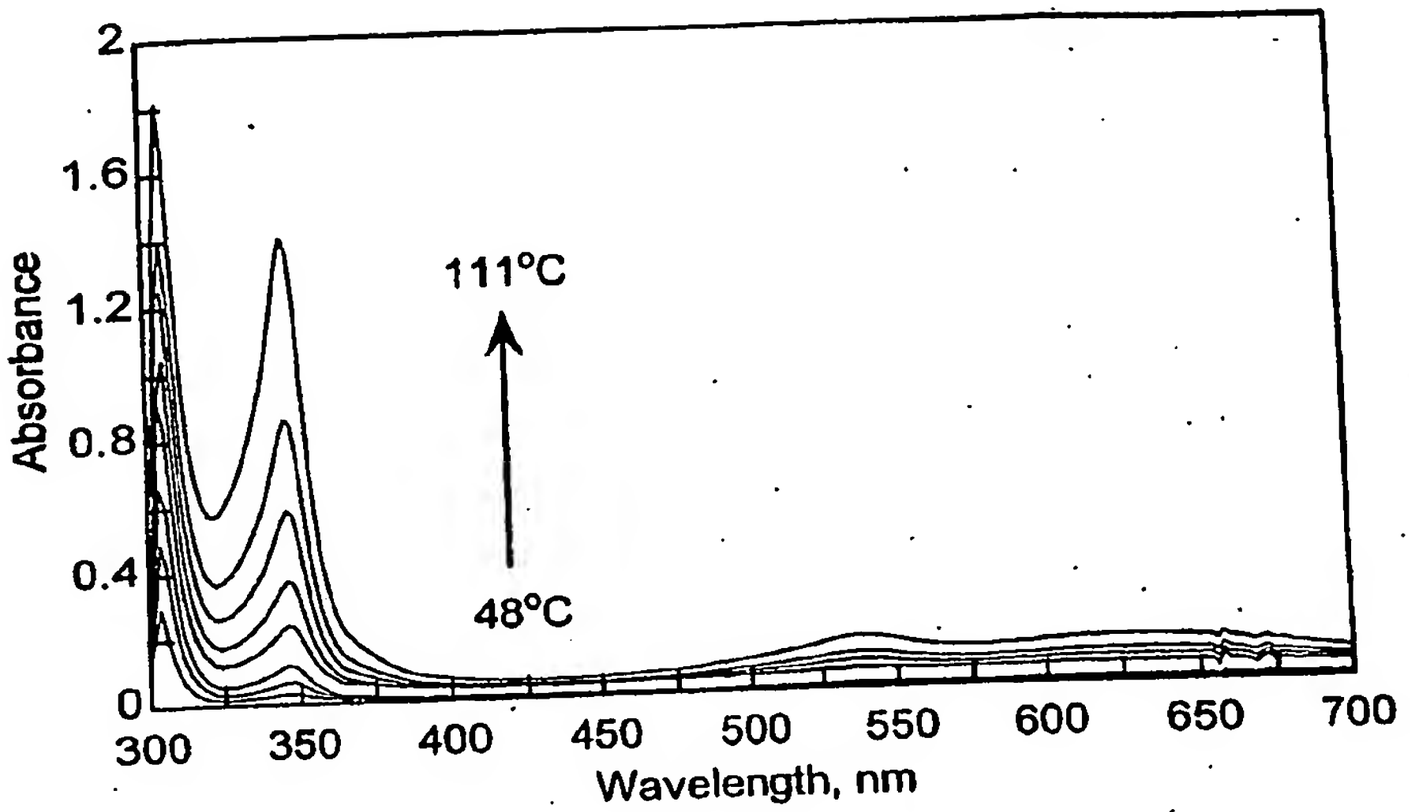

Absorbance
2
1.6
1.2
0.8
0.4
0
111°C
48°C
300
350
400
450
500
550
600
650
700
Wavelength, nm

Figure 2

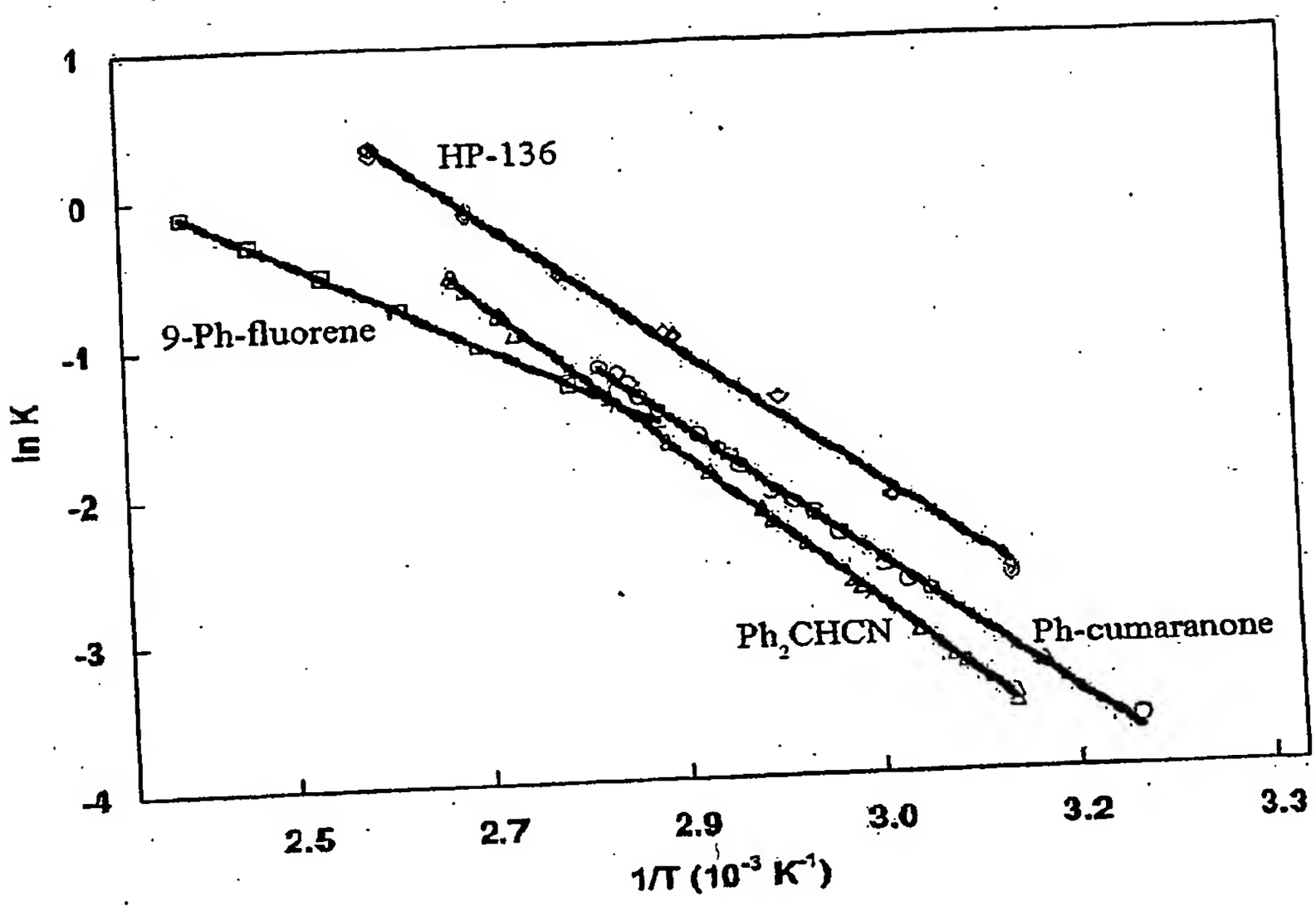

1
0
-1
-2
-3
-4
ln K
HP-136
9-Ph-fluorene
Ph2CHCN
Ph-cumaranone
2.5
2.7
2.9
3.0
3.2
3.3
1/T (10-3 K-1)

Figure 3a

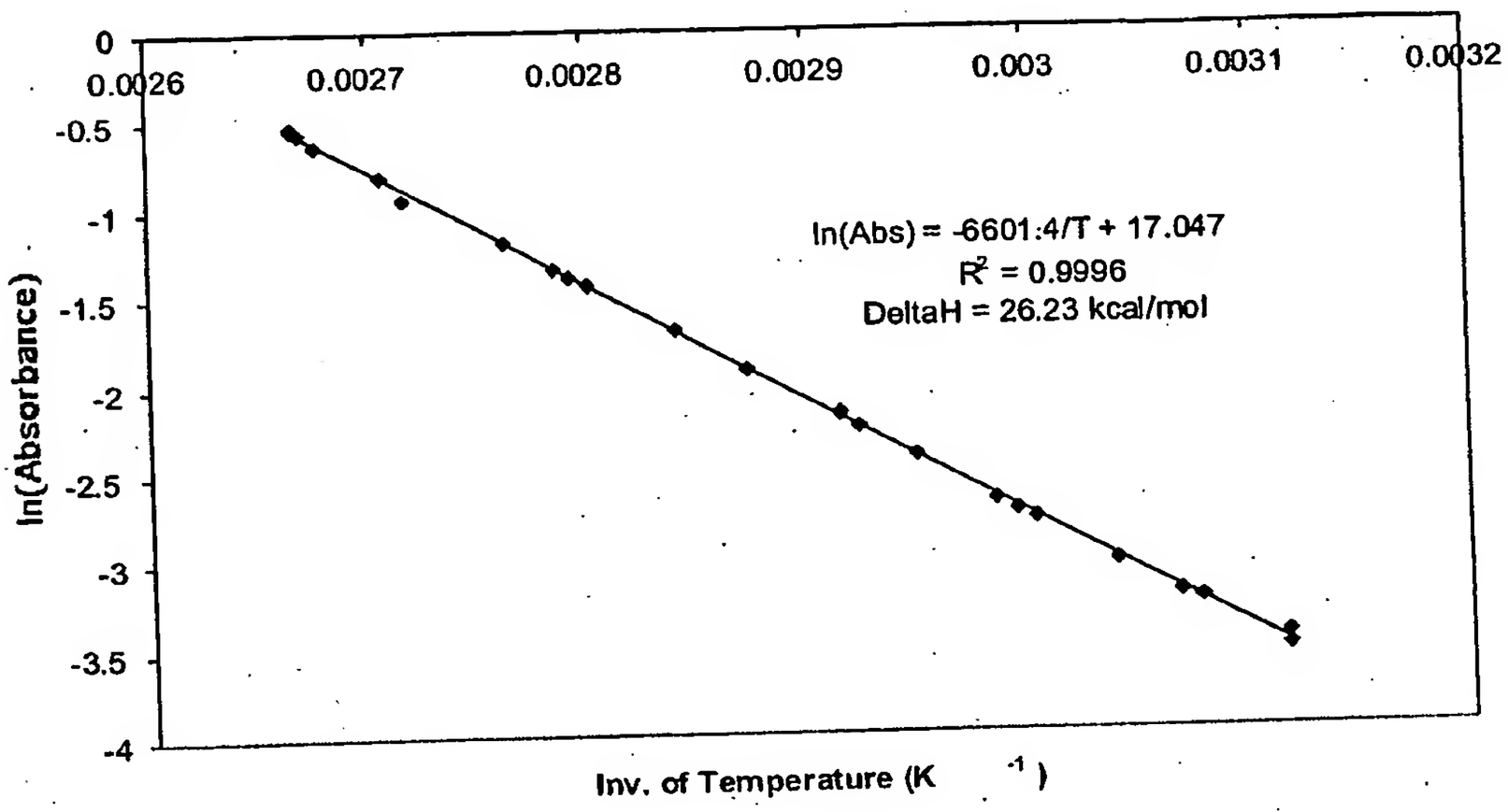

0
0.0026
0.0027
0.0028
0.0029
0.003
0.0031
0.0032
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
ln(Absorbance)
ln(Abs) = -6601.4/T + 17.047
R2 = 0.9996
DeltaH = 26.23 kcal/mol
Inv. of Temperature (K -1)

Figure 3b

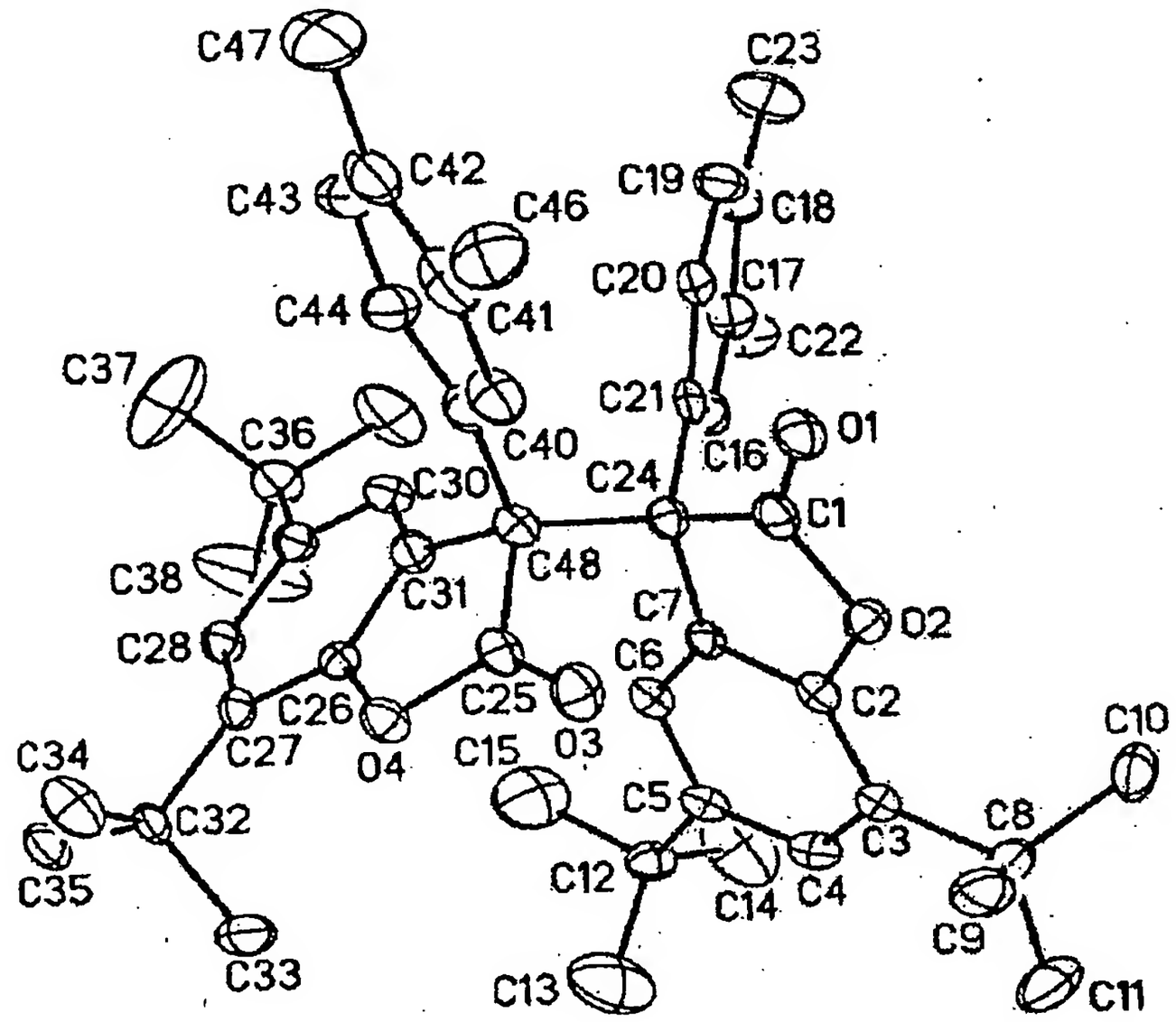

C47
C23
C42
C43
C46
C19
C18
C44
C41
C20
C17
C22
C37
C21
C36
C40
C16
O1
C30
C24
C1
C38
C31
C48
C7
O2
C28
C6
C26
C25
C2
C10
C34
C27
O4
C15
O3
C5
C8
C32
C12
C3
C35
C14
C4
C9
C33
C13
C11

Figure 4

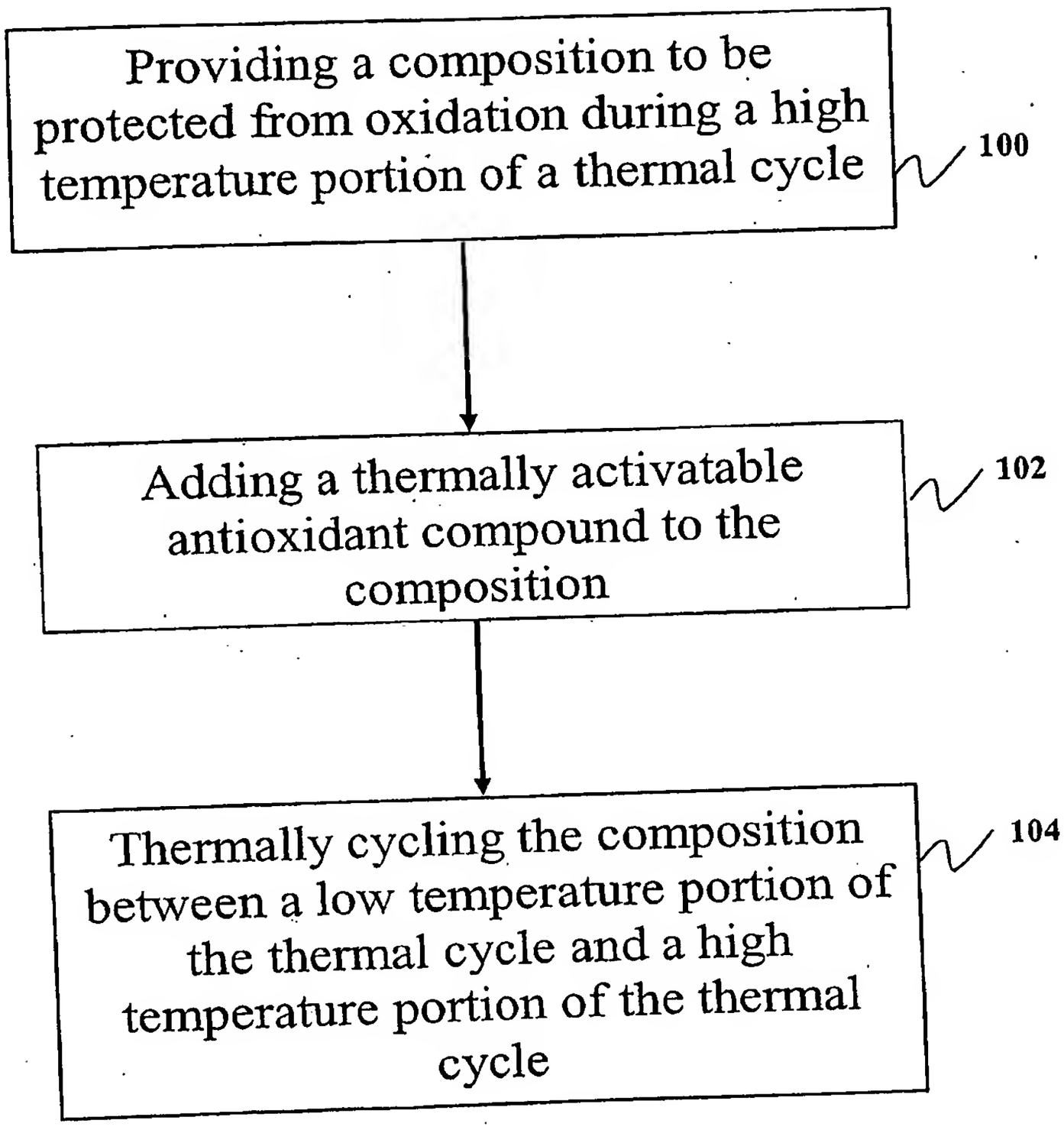

Providing a composition to be protected from oxidation during a high temperature portion of a thermal cycle
100
Adding a thermally activatable antioxidant compound to the composition
102
Thermally cycling the composition between a low temperature portion of the thermal cycle and a high temperature portion of the thermal cycle
104

Figure 5

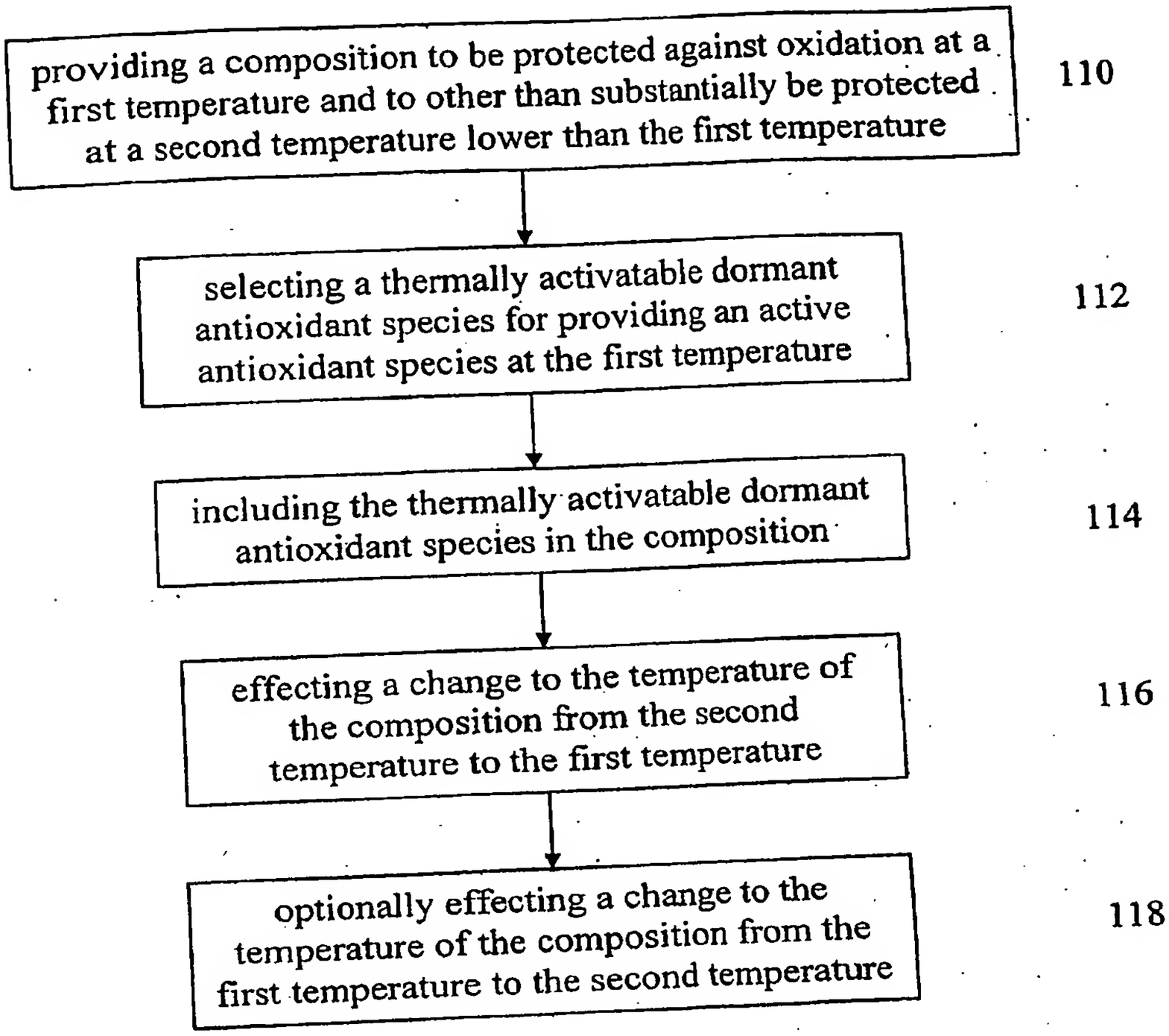

providing a composition to be protected against oxidation at a first temperature and to other than substantially be protected at a second temperature lower than the first temperature
110
selecting a thermally activatable dormant antioxidant species for providing an active antioxidant species at the first temperature
112
including the thermally activatable dormant antioxidant species in the composition
114
effecting a change to the temperature of the composition from the second temperature to the first temperature
116
optionally effecting a change to the temperature of the composition from the first temperature to the second temperature
118

Figure 6

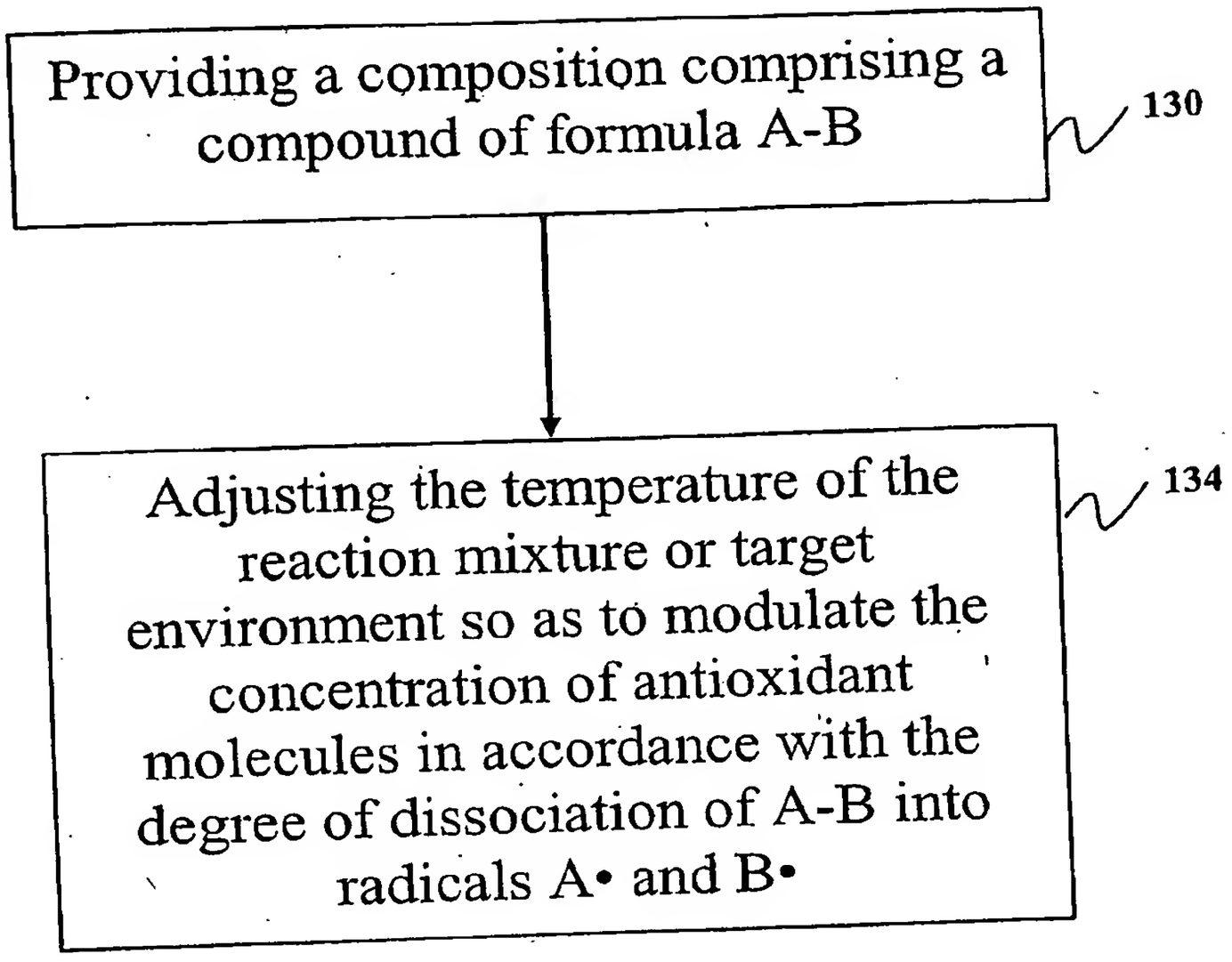

Providing a composition comprising a compound of formula A-B
130
Adjusting the temperature of the reaction mixture or target environment so as to modulate the concentration of antioxidant molecules in accordance with the degree of dissociation of A-B into radicals A• and B•
134

Figure 7

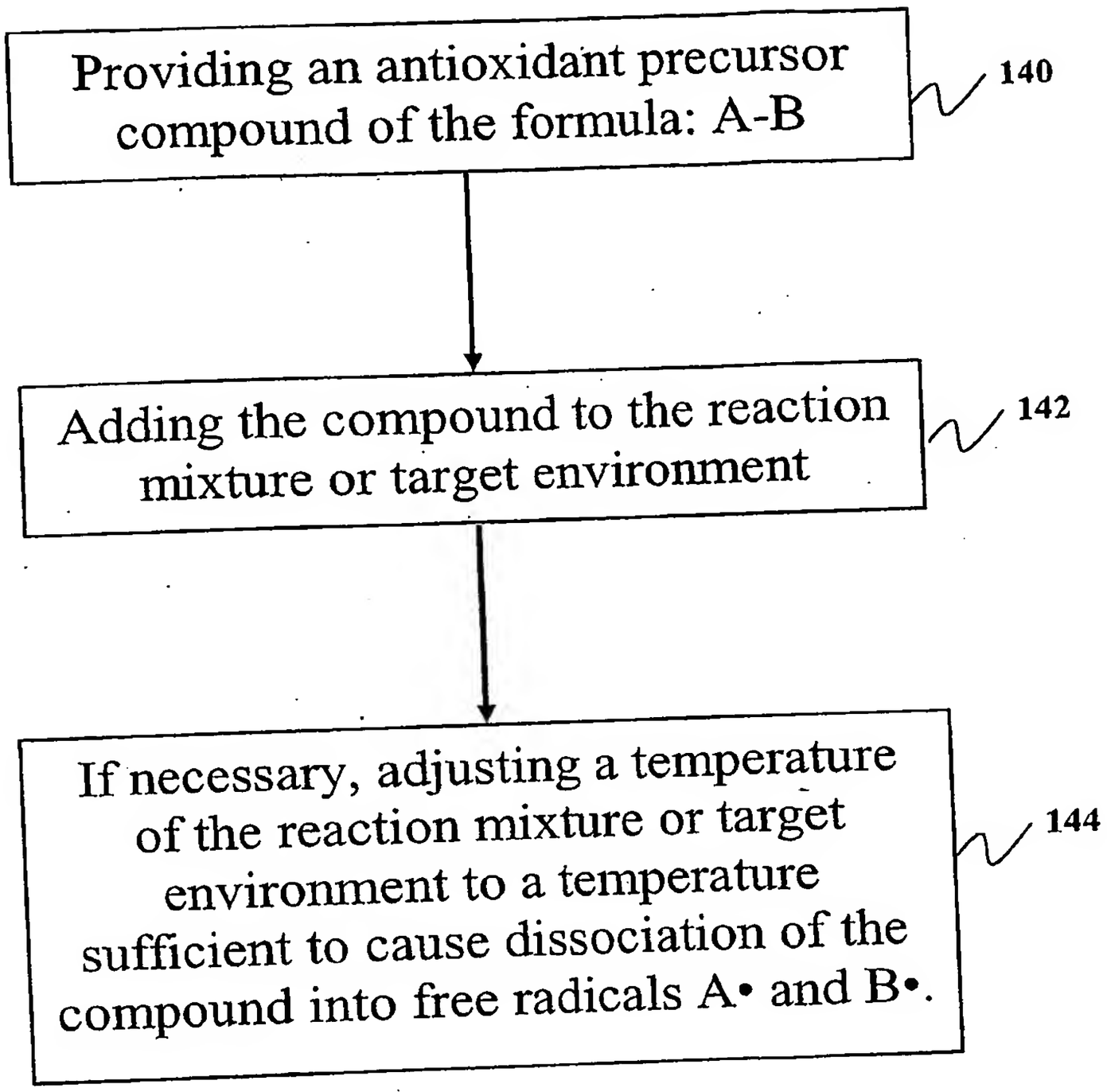

Providing an antioxidant precursor compound of the formula: A-B
140
Adding the compound to the reaction mixture or target environment
142
If necessary, adjusting a temperature of the reaction mixture or target environment to a temperature sufficient to cause dissociation of the compound into free radicals A• and B•.
144

Figure 8

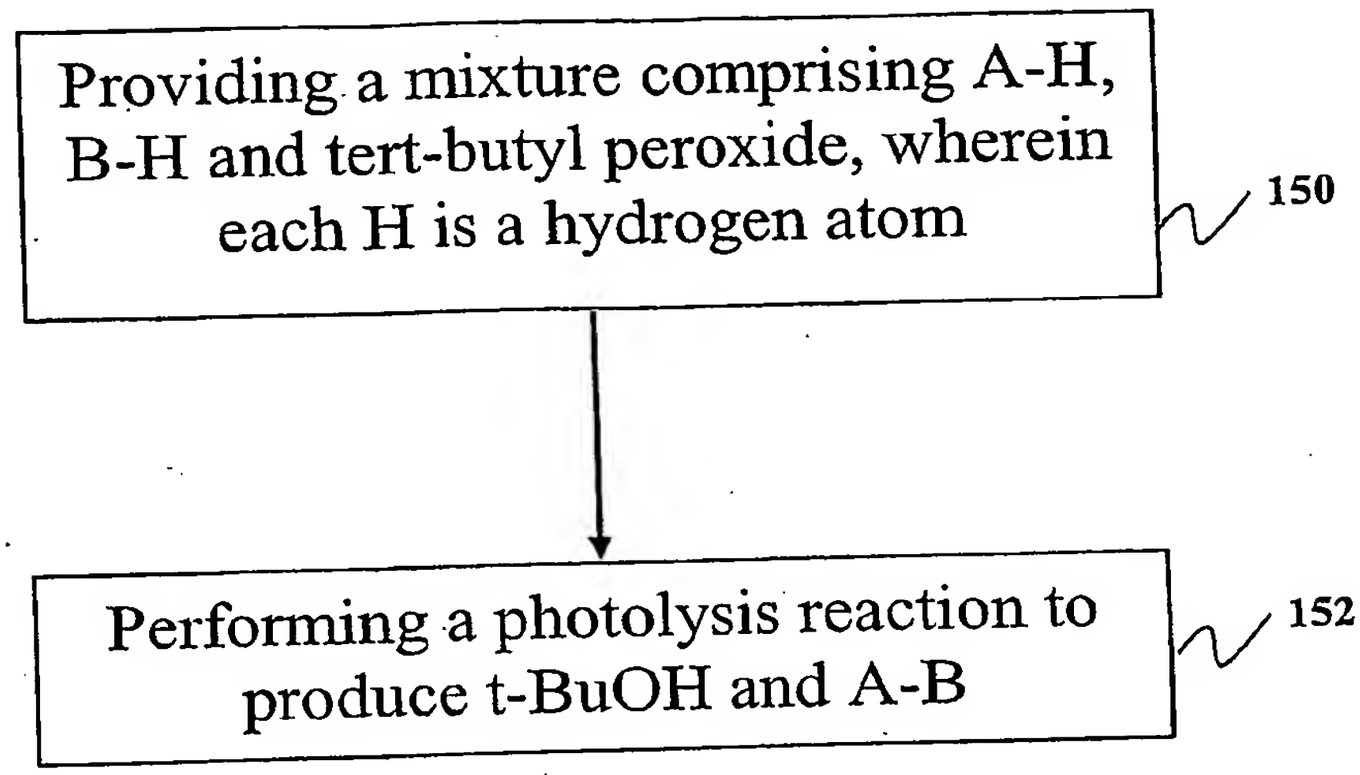

Providing a mixture comprising A-H, B-H and tert-butyl peroxide, wherein each H is a hydrogen atom
150
Performing a photolysis reaction to produce t-BuOH and A-B
152

Figure 9

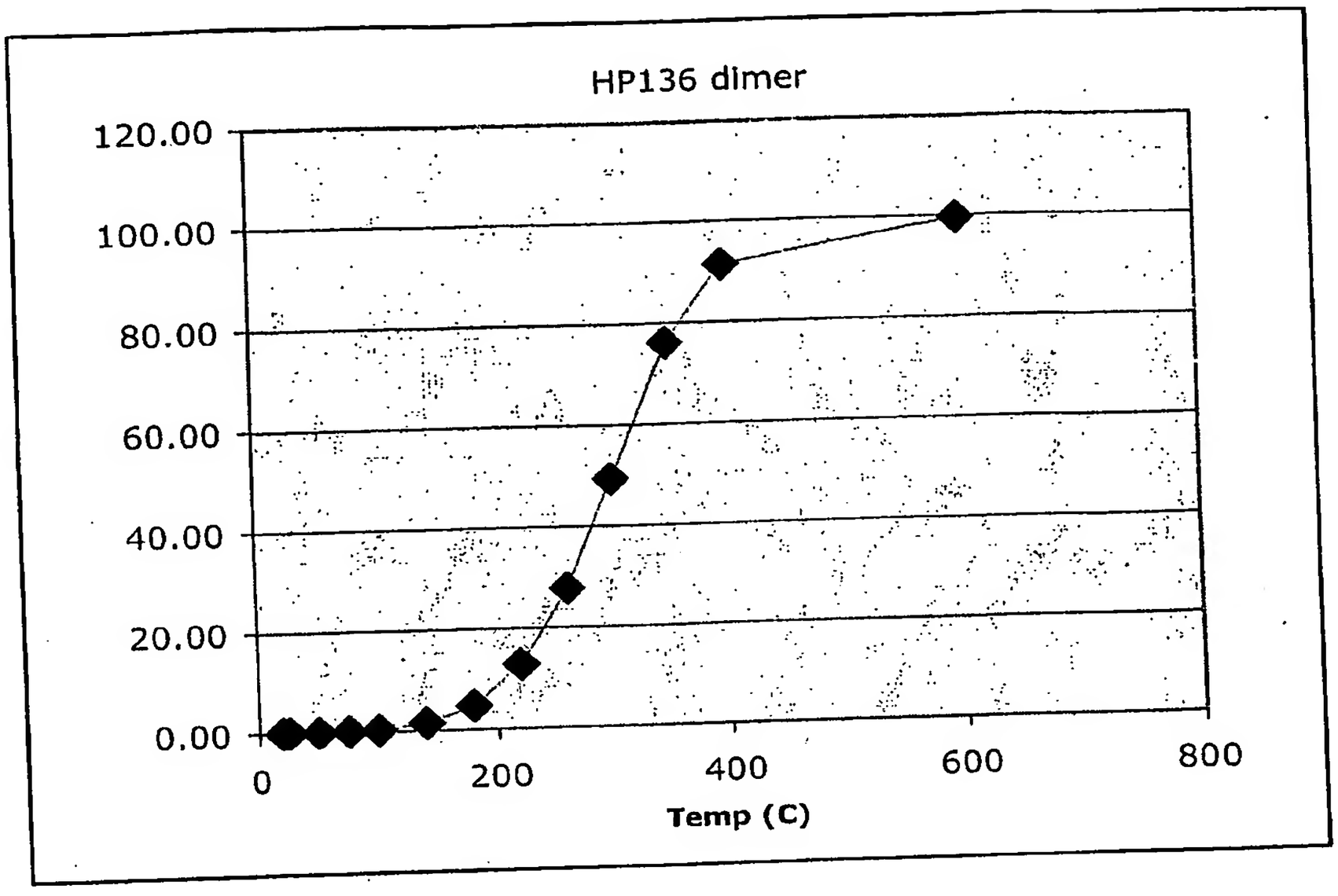

HP136 dimer
120.00
100.00
80.00
60.00
40.00
20.00
0.00
0
200
400
600
800
Temp (C)

Figure 10

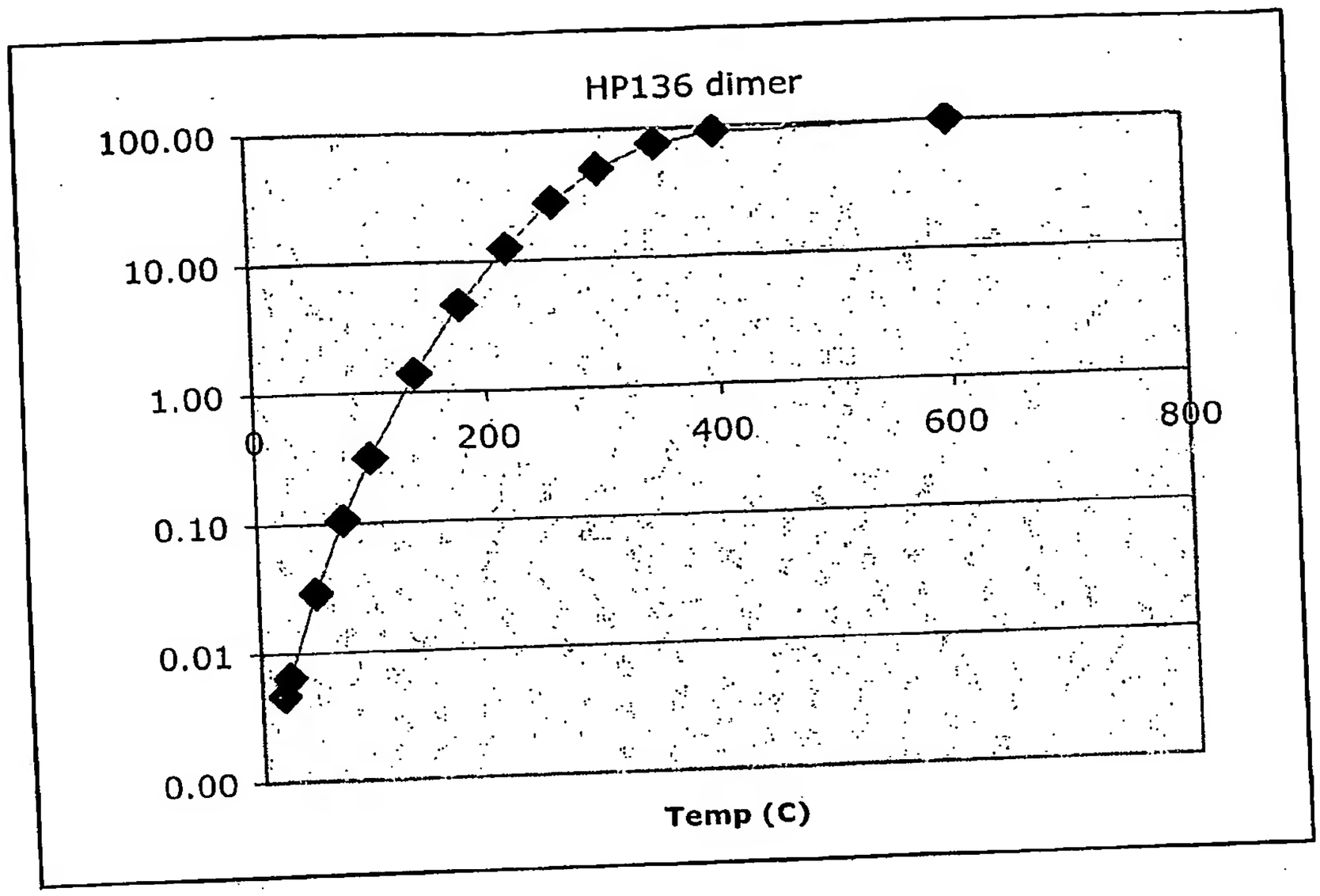


Figure 11